Improved quantification of livestock associated odorous volatile organic compounds in a standard flow-through system using solid-phase microextraction and gas chromatography - mass spectrometry

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Abstract. Aerial emissions of odorous volatile organic compounds (VOCs) are an important nuisance factor from livestock production systems. Reliable air sampling and analysis methods are needed to develop and test odor mitigation technologies. Quantification of VOCs responsible for livestock odor remains an analytical challenge due to physicochemical properties of VOCs and the requirement for low detection thresholds. A new air sampling and analysis method was developed for testing of odor/VOCs mitigation in simulated livestock emissions system. A flow-through standard gas generating system simulating odorous VOCs in livestock barn emissions was built on laboratory scale and tested to continuously generate ten odorous VOCs commonly defining livestock odor. Standard VOCs included sulfur VOCs (S-VOCs), volatile fatty acids (VFAs), and *p*-cresol. Solid-phase microextraction (SPME) was optimized for sampling of diluted odorous gas mixtures in the moving air followed by gas-chromatography mass-spectrometry (GC-MS) analysis. CAR/PDMS 85 µm fiber was shown to have the best sensitivity for the target odorous VOCs. A practical 5-min sampling time was selected to ensure maximum extraction of VFAs and *p*-cresol, as well as minimum displacement of S-VOCs. Method detection limits ranged from 0.392 to 2.64 ppbv for S-VOCs, 0.233 to 0.767 ppbv for VFAs, and 0.308 ppbv for *p*-cresol. The method developed was applied to quantify VOCs and odorous VOC mitigation with UV light treatment. The measured concentrations ranged from 20.1 to 815 ppbv for S-VOCs, 10.3 to 315 ppbv for VFAs and 4.73 to 417 ppbv for *p*-cresol. Relative standard deviations between replicates ranged from 0.67% to 12.9%, 0.50% to 11.4%, 0.83% to 5.14% for S-VOCs, VFAs and *p*-cresol, respectively. This research shows that a simple manual SPME sampler could be used successfully for quantification of important classes of odorous VOCs at concentrations relevant for real aerial emissions from livestock operations.

Key words: VOCs, SPME, GC-MS, odor, air sampling, standard gas generation system

1. Introduction

Worldwide proliferation of intensive large-scale livestock production systems has focused the attention on aerial emissions of odor, VOCs, NH_3, H_2S, and bioaerosols, including pathogens [1]. Livestock air emissions are a complex mixture of very dilute odorous VOCs, among which several key volatile organic compounds (VOCs and semi-VOCs) were found to be responsible for odor nuisance [2-8]. Previous studies reported three main categories of chemicals as the key odorants from swine operations, i.e., sulfur-containing VOCs (S-VOCs), volatile fatty acids (VFAs), and phenolics/indoles [2,8]. Ammonia, which is characterized by relatively higher odor threshold compared to most of these VOCs, and typically present at higher concentrations, may or may not correlate with odor concentrations [9]. Hydrogen sulfide and methanethiol were reported to represent 70 to 97% of the total sulfuric gases and volatiles in manure [10]. The most dominant sulfuric gases and volatiles in cattle manure were found to be hydrogen sulfide (39%), methanethiol (34%) and dimethyl sulfide (21%) [11]. VFAs were reported to be major odorants for emissions associated with animal production systems, more specifically, about 60% of total VFAs in manure were present as acetic acid, followed by propanoic acid, butyric acid, isobutyric acid and isovaleric acid [12-14]. Bulliner et al. [2] reported *p*-cresol as the key compound responsible for the characteristic smell of swine odor. It is generally accepted that the key odorous VOCs responsible for livestock odor typically present at very low levels (ppbv to pptv).

Quantification of odorous VOCs from livestock operations is necessary in order to develop and test various odor mitigation technologies. However, there are challenges in quantifying target odorous VOCs because of their low concentrations (typically in the ppbv range) and the extremely low odor threshold of some of these compounds (which can be in the pptv range). Moreover, the majority of odorous VOCs are present at such trace levels in a complex matrix of odor-insignificant volatiles.

Several studies reported analytical detection limits of livestock odorants (Table 1). However, most of these were done in a static system; fewer studies aimed at quantifying VOCs in livestock air applying flow-through systems [15]. Moreover, in most studies summarized in Table 1, samples were stored in a polymeric bag (e.g. Tedlar) or a metal canister [19]. Such storage devices were reported to suffer from sample contamination and sample loss [26]. Finally, most of reported studies focused on a few target compounds, such

as S-VOCs or VFAs only.

Notably, human odor detection threshold of target VOCs selected in the present study were reported at very low concentrations, mostly below 4 ppbv except acetic (145 ppbv) and propanoic acid (35.5 ppbv), as shown in Table 2. To fulfill the experimental needs, a system capable of producing gas mixtures at such low concentrations is required and an appropriate sampling and analytical method has to be established to achieve method detection limits (MDLs) as low as possible.

A method for sampling and analysis of odorous VOCs in moving air simulating concentrations present in exhaust air of livestock barns was optimized in this study. This method is based on solid-phase microextraction (SPME) coupled with gas chromatography-mass spectrometry (SPME-GC-MS). A mixture of 10 standard odorous VOCs was used to simulate air emissions of livestock barns. As an illustration of the application of this analytical method, the simulating gas mixture was treated in a flow-through reactor with UV light, thus lowering concentrations further and challenging the method for residual concentrations as well.

2. Materials and methods

2.1. Standards and reagents

HPLC-grade standards of S-VOCs, VFAs and *p*-cresol were purchased from Sigma-Aldrich (Milwaukee, WI).

2.2. Standard gas generation system

A standard gas generation system (SGG; Fig. 1) was built to generate mixtures of VOCs/H_2S at concentrations typical to air emissions from livestock barns. Chemicals used included H_2S and S-VOCs (methyl mercaptan, ethyl mercaptan, butyl mercaptan and dimethyl sulfide (DMS)), VFAs (acetic, propanoic, butyric and isovaleric acid), and a phenolic compound (*p*-cresol). These target compounds are generally liquids at room temperature; thus permeation tubes were used. Each chemical was generated by one permeation tube (made and calibrated in-house or purchased from KIN-TEK™ Laboratories (La Marque, TX, USA)). All permeation tubes were made from Teflon. The permeation is a process of the gas

dissolving into the Teflon wall and evaporating from the outer surface, which is highly sensitive to temperature. The emission rate of each permeation tube was controlled by temperature [31,32].

Standard gas concentrations of each compound were calculated based on the emission rate (E) of the permeation tube, which was determined by equation 1,

$$E = \frac{\Delta m}{t} \quad (1)$$

Where *E* (ng/min) is the emission rate of each compound, Δm (ng) is the average mass loss between two weighing times, and *t* (min) is the permeation period. The concentration of each compound was estimated using equation 2,

$$C_{gas} = \frac{E}{Q} \quad (2)$$

Where C_{gas} is the concentration of compound of interest (ng/mL), Q is air flow rate in the system (mL/min).

To be comparable with most literature data, gas concentration were converted to volume concentration by equation 3,

$$C_{ppm} = C_{gas} \times \frac{R \times T}{MW \times P} \quad (3)$$

Where C_{ppm} is gas concentration in parts per million (ppmv), *R* is ideal gas law constant, *R*= 8.314 (m^3 Pa K^{-1} mol^{-1}), *P* and *T* are atmospheric pressure (*P*=101.32 kPa under atmospheric conditions) and temperature (K), respectively, and *MW* is the molecular weight of each compound (g/mol). Since experimental conditions were normalized to *T*=298 (K) (25 ºC), and *P*=101.32 (kPa). Equation 3 can be simplified to equation 4

$$C_{ppm} = C_{gas} \times \frac{8.314 \times 298}{MW \times 101.32} = 24.4 \times \frac{C_{gas}}{MW} \quad (4)$$

Where C_{gas} was gas concentration in ng/mL calculated from Eq. 2.

Under constant temperature, different gas concentrations could be achieved by changing the airflow, according to Equation (2). Successful generation of constant VOCs (VFAs and phenolics) emissions at trace levels deploying the permeation tube technology was reported previously [35].

Differing concentrations were achieved by changing the air flow rate, i.e., the maximum concentration corresponding to 300 mL/min of air flow and the minimum concentration corresponding to 5000 mL/min (Table 2). The carrier gas was 99.995% pure air (pure oxygen or pure nitrogen are optional carrier gases based on experimental needs). These concentrations were controlled precisely using mass flow controllers (Aalborg, Orangeburg, NY). The stability of generating consistent standard gas was checked by running gas samples daily (n=3) and continuously for 44 days. Stability was validated, as the deviation between days within the experimental period for all target analytes was small (<10%). A summary of gas concentrations and physicochemical properties for all target compounds is presented in Table 2.

This system successfully simulated the continuous emissions of VOCs from livestock operations at their typical ranges of concentrations [16]. Gas concentrations generated fell into or were very close to the typical range of odorant concentrations emitted from livestock swine facilities in North Carolina (0.075 mg/m^3 (30.5 ppbv) for acetic acid, 0.04 mg/m^3 (13.2 ppbv) for propanoic acid, 0.22 mg/m^3 (60.9 ppbv) for butyric acid and 0.015 mg/m^3 (4.15 ppbv) for isobutyric acid; 0.041 mg/m^3 (9.25 ppbv) for *p*-cresol) as reported by Schiffman et. al. [22]. Emissions of *p*-cresol from dairy farms was reported to be in the range of 0.6~100 μg·m^{-3} [23] which can be converted to 0.14~23.8 ppbv, assuming atmospheric conditions. Not much information about measured concentrations of sulfur VOCs was found in the literature, probably because field concentrations were below their detection threshold [22], while a range of 0.064-0.927 ppbv was reported for dimethyl sulfide emitted from a slurry wastewater lagoon [18].

2.3. Headspace solid phase microextraction (HS-SPME)

All HS-SPME extractions were performed with a SPME fiber coupled with a manual holder from Supelco (Bellefonte, PA, USA). Before use, each fiber was conditioned in a heated GC splitless injection port at 260 °C under helium flow. After conditioning, SPME fiber was quickly moved to the sampling ports to perform extractions as required. Once air samples were collected, the SPME fiber was removed and immediately transferred to the injection port of the GC for analysis. The desorption time of SPME fiber was set to 10 min at 260 ºC. All SPME extractions were completed at constant temperature (see section 2.5). The sampling time was optimized (described in section 2.6).

2.4. SPME fiber selection

Four SPME fiber coatings, Carboxen/polydimethylsiloxane (CAR/PDMS) 85 µm, PDMS/divinylbenzene (DVB0 65 µm, polyacrylate (PA) 85 µm and PDMS 100 µm were examined in this work to select a fiber coating with the best extraction efficiency on target VOCs. All samples were taken in triplicate at 25 ºC from SGG by headspace SPME fiber. Carrier air was dry. Gas flow rate was set constant at 300 mL/min.

Fiber selection was conducted for standard odorous gases in the SGG to select the SPME coating with best trapping capacity of target analytes. This part was done within 48 h with constant airflows and temperature (constant gas concentrations) in the SGG. Three replicated samples were taken continuously for each fiber coating. The sampling time was 5 min (Section 2.6).

2.5. Sampling time optimization

Out of the four fiber coatings, CAR/PDMS 85 µm was chosen for the optimization of sampling time. Sampling times of 1, 3, 5, and 10 min were examined for standard odorous gases in the SGG with triplicates. Partitioning coefficient, molecular size and boiling point are considered important factors influencing equilibration time [37]. Since the CAR/PDMS phase is adsorptive [38], sampling time was optimized by selecting the longest extraction time before fiber sorptive capacity limits the rate of analyte extraction.

2.6. Method application to photoreactor

The developed method was challenged by applying it to odor mitigation technology by means of a photoreactor. The effluent from the SGG (Section 2.2) was fed to a flow through chamber which was used as the photoreactor using variable numbers of low-pressure Hg lamps (principle output at 254 nm, with other characteristic bands at 185, 312 and 365 nm). The reactor contained TiO_2 as photocatalyst, and included a temperature control sensor, and an on/off switch. When the UV source was on, photodegradation of gases was induced. When the UV light was off, the photoreactor functioned simply as a flow through cell. More details about the UV photoreactor are described in Yang et al. [36]. Sampling ports were located before and after the photoreactor to allow sampling of untreated and treated flow of standard gas mixtures

(shown in Fig. 1). All samples were taken in triplicates, while six replicates were used for method validation.

2.7. Analytical methods

2.7.1 Chemical and odor analysis: GC-MS

A conventional GC–MS (Agilent 6890N GC/5973 MS from Agilent, Wilmington, DE, USA) was utilized in this study. A non-polar pre-column and a polar column were installed in series in the system. All samples were analyzed by the system under the following configuration conditions: injector 260 °C; FID, 280 °C, column oven, 40 °C initial, 3 min hold, 7 °C /min, 220 °C final, 10 min hold. Carrier gas was helium. Mass (molecular weight)-to-charge ratio (*m*/*z*) range was set between 33 and 280. Spectra were collected at 6 s and electron multiplier voltage was set to 1000 V. The MS detector was auto-tuned weekly.

Target compounds in this work were sampled and run on to GC-MS for analysis. Retention time (RT) was determined for each compound. To improve accuracy, single ion mode (SIM) was used when identification of compounds was not required. Identification was needed for the treated gases, and compounds were positively identified by two criteria: (1) the retention time on the GC capillary column, and (2) the match between the mass spectra of analyte and standard spectra in MS library from Bench-Top/PBM (from Palisade Mass Spectrometry, Ithaca, NY, USA). VOC abundance was measured as area counts under the MS peak.

2.7.2 Linearity, repeatability and method detection limit (MDL)

The new method repeatability was estimated at different standard gas concentrations by varying air flow rate in SGG, including five levels for sulfur VOCs, nine for VFAs, and eleven for *p*-cresol. All tests were conducted in triplicate, except at air flow of 500 mL/min (conducted in 7 replicates), when MDL was estimated. The quantification of target VOCs was completed by establishing calibration curves deploying the standard gas concentrations. The repeatability and the calibration curves were studied under the optimized SPME conditions. All extractions were done under experimental conditions of 25 °C, dry air, 5 min sampling time and using CAR/PDMS 85 µm fiber. Precisely controlled air flow varied from 300 to 2300 mL/min. Data were analyzed and compared using means and relative standard deviations

(RSDs).. MDL was calculated based on the US Environmental Protection Agency (EPA) methodology [40]. The MDLs were defined as the minimum concentration of a substance that can be measured and reported with 95% confidence when the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The MDLs for target compounds were estimated using equation 5,

$$MDL = s \times t_{(n-1,\ 1-\alpha)} \quad (5)$$

where n = number of replicates. Replicates with standard analytes at concentration 1–5 times greater than the estimated MDL were generated from the SGG system; s = standard deviation of measured concentrations of n spike determinations, t = Student's t-value at $n-1$ degree of freedom and $1-\alpha$ (equals to 95%) confidence level. In this work, n=7 replicates (t-value=2.57) for *p*-cresol and n= 6 replicates (t-value=2.45) for all other target VOCs.

2.7.3 Statistical analysis

Detection limit and repeatability data were analyzed using the statistical package JMP v. 10.0.0 (SAS Institute, Inc., Cary, NC). Data were subject to a one-way analysis of variance (ANOVA). Correlation coefficients of the calibration curves and *p*-values between sample extractions with different fibers were calculated with Microsoft Excel.

3. Results and discussion

3.1 SPME fiber selection

Comparison of extraction efficiency of target VOCs for CAR/ PDMS 85 µm, PDMS/DVB 65 µm, PA 85 µm and PDMS 100 µm SPME coatings is illustrated as MS detector response for each compound in Fig. 2 (Table S1, Supplemental Material). All the four SPME fiber coatings performed sufficiently effective extraction on all selected VOCs except of sulfur compounds. More effective extraction was observed using CAR/PDMS 85 µm and PA 85 µm fiber coatings than the other two for all target compounds, except for *p*-cresol, for which PDMS/DVB 65 µm was superior. Comparison between the mixed phase coating CAR/PDMS 85 µm and the single phase coating PA 85 µm indicated that CAR/PDMS 85 µm would be a better choice due to: 1) more effective extraction of all target compounds except DMS; 2) consistency with

one of the selection guidelines [38] that mixed phase coatings are considered to fit volatile compounds sampling better than single phase coatings. One of the odor indicators for swine manure is *p*-cresol [2,6,39], whose extraction efficiency is considered very critical. However, the difference in extraction efficiency between CAR/PDMS 85 µm and PDMS/DVB 65 µm on *p*-cresol was not statistically significant (p=0.166), while very significant difference (p=0.009) was observed for these two coatings in extracting S-VOCs and VFAs. CAR/PDMS 85 µm captured more VFAs than PDMS/DVB 65 µm under the same conditions. Hence, CAR/PDMS 85 µm coating can be more effective in extracting a wider range of compounds. PDMS/DVB 65 µm also had a poor performance in trapping S-VOCs. Sulfur VOCs at trace levels, even below the detection limit, contribute significantly to the total odor [25], and is another critical group of VOCs associated with livestock odors. According to Pawliszyn [38], one important principle in developing methodology is that the primary consideration should be given to the group of analytes that is most difficult to extract and should be based on overall extraction efficiency. Hence CAR/PDMS 85 µm coating was selected to do all the following extractions in this study.

The fiber selection was further justified by comparing the MS detector response RSD (%) ranges to standard concentrations of target VOCs sampled with four SPME fibers (Table 3). The RSD (%) ranged from 4.9% to 19.3% for the four fibers used. The relatively small RSD associated with the use of CAR/PDMS 85 µm coating showed good reproducibility and more stable performance for all extractions. The RSD range (from 3.3% to 7.8%) was more favorable compared with that for all the other fiber coatings.

3.2. Selection of sampling time

The sampling time optimization was conducted for CAR/PDMS 85 µm fiber. Experiment was performed in triplicates at a 5-point time series basis ranging from 1 min to 1 h. The mean FID response was plotted against extraction time. Detected peak area (PA) counts increased with sampling time in a linear trend for most compounds except for methyl mercaptan after 10 min extraction, when it started to deviate from linearity. However, when up to 10 min was selected, all target odorants showed a high positive linearity between extracted mass and extraction time (Fig. 3). The correlation coefficient R^2 values for VFAs and *p*-cresol nearly equal to 1 (Table 4). According to Pawliszyn [38], the practical sampling time should be

the longest extraction time with the maximum amount extracted before the extraction reaches equilibrium. However, CAR/PDMS extracts analytes by adsorption, which means a competitive adsorption of VOCs to the surface of the fiber coating. With lower affinity to CAR/PDMS, S-VOCs tend to be easily replaced. None of previous research analyzed S-VOCs, VFAs and *p*-cresol simultaneously, thus not dealing with a range of molecular weight compounds and functionalities with differing affinities to the fiber. Efficient extraction of S-VOCs in a complex gas mixture (of target VOCs) needs to be assured. Non-linear extraction conditions for S-VOCs are less useful for quantification, are difficult to control and not recommended for quantitative analysis. A shorter extraction time in a linear extraction range was considered. Good reproducibility was observed for target VOCs (RSD less than or close to 5%) for up to 5 min extraction (Table 4), and, at the same time, the risk of non-linear extractions and fiber coating saturation was minimized. This shorter extraction time (5 min) is also more practical in the sense of time saving for sampling. Hence 5 min extraction was chosen for most of the analyses in this work.

Further comparison was illustrated by plotting the FID detector response normalized by gas concentrations over sampling time for each compound (Fig. 3). The slope m represents FID response normalized by gas concentrations as a function of air sampling times with SPME. The relationship between normalized peak area (PA) counts and sampling time followed four salient trends: 1) comparison among all three groups (S-VOCs, VFAs and *p*-cresol) showed that the slope m* increased with molecular weight except for ethyl mercaptan/DMS and the isomer isovaleric acid; 2) comparison within each group showed a steadily, if not linearly, increasing trend between the slope m* and molecular weight except for isovaleric acid as shown in Fig. S1, and the correlation coefficients were 0.96 and 1.00 for S-VOCs and VFAs, respectively; 3) more rapid increase was observed for VFAs than S-VOCs compounds; 4) *p*-cresol was the compound with much higher m* than the other analytes. RSD (%) and linearity of FID response to standard concentrations of target VOCs sampled with SPME fiber at different air sampling times are summarized in Table 4.

3.3. Method evaluation and validation

The optimized procedure was evaluated and validated based on its linearity, detection limit, repeatability and recovery. The linearity of the method was evaluated by preparing

calibration standards generated by SGG. The calibration curves were linear over the concentration ranges of target analytes as shown in Fig. 4. The linear regression equation coefficients, range of the gas concentrations, R^2, method detection limits (MDLs) and ranges of RSDs (%) are summarized in Table 5. MDLs were estimated based on 6 replicates (7 for *p*-cresol). Up to 1 ppbv MDL was achieved for most of the compounds except methylmercaptan and ethylmercaptan. The lowest MDL was 0.233 ppbv for butyric acid, while the MDL of *p*-cresol was 0.308 ppbv, which covers the range of typical aerial concentration of *p*-cresol in livestock emissions [16, 41].

3.4. Method application for analysis of odorous VOCs in moving air irradiated with UV

An example of a total ion chromatogram of UV treated gas sample from SGG is shown in Fig. 5. VOC concentrations were calculated using the calibration curves (Table 6). The concentrations of all VOCs were in the range of the maximum measured concentrations calculated by calibration curves and the MDLs. In this demonstration of odor mitigation by means of UV, measured concentrations of key odorants were reduced by approximately 40 to 70%.

4. Conclusions

Headspace-SPME coupled with GC–MS is a useful and effective analytical tool for characterization and quantification of complex odorant mixtures associated with livestock operations. The low detection limits (ranging from 0.23 to 2.64 ppbv) obtained with the optimized method were approximately one order of magnitude below published detection thresholds for target odorous gases.

Extraction of sulfur VOCs, VFAs and *p*-cresol with SPME were optimized simultaneously for the first time. The CAR/PDMS 85 µm extraction efficiency was positively correlated with molecular weight of target compounds of the same chemical functionality. Methyl mercaptan, ethyl mercaptan, and dimethyl mercaptan at low molecular weights have the lowest affinity to the SPME fiber. Extraction efficiency of these compounds with low affinity to SPME fiber was optimized by shortening extraction time.

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References

[1] Yates, S.R., McConnell, L.L., Hapeman, C.J., Papiernik, S.K., S. Gao, S.L. Trabue. 2011. Managing Agricultural Emissions to the Atmosphere: State of the Science, Fate and Mitigation, and Identifying Research Gaps. J. Environ. Qual. 40:1347–1358.

[2] Bulliner E.A., J.A. Koziel, L. Cai, D. Wright. 2006. Characterization of livestock odors using steel plates, solid phase microextraction, and multidimensional - gas chromatography-mass spectrometry-olfactometry. Journal of the Air & Waste Management Association, 56: 1391-1403.

[3] Cai, L., J.A. Koziel, J. Davis, Y.C. Lo and H. Xin. 2006. Characterization of VOCs and odors by in vivo sampling of beef cattle rumen gas using SPME and GC-MS-olfactometry. Anal. and Bioanal. Chem., 386(6): 1791-1802.

[4] Cai, L., J.A. Koziel, A.T. Nguyen, Y. Liang and H. Xin. 2007. Evaluation of zeolite for control of odorants emissions from simulated poultry manure storage. J. Environ. Qual., 36(1): 184-193.

[5] Lo, Y. C., J.A. Koziel, L. Cai, S.J. Hoff, W.S. Jenks, H. Xin. 2008. Simultaneous chemical and sensory characterization of VOCs and semi-VOCs emitted from swine manure using SPME and multidimensional gas chromatography-mass spectrometry-olfactometry system. J. of Environ. Qual., 37(2): 521-534.

[6] Wright, D., L. Nielsen, D. Eaton, F. Kuhrt, J.A. Koziel, J.P. Spinhirne, D.B. Parker. 2005. Multidimensional GC-MS-olfactometry for identification and prioritization of malodors from confined animal feeding operations. Journal of Agricultural and Food Chemistry. 22: 8663-8672.

[7] Zhang, S., L. Cai, J.A. Koziel, S.J. Hoff, D.R. Schmidt, C.J. Clanton, L.D. Jacobson, D.B. Parker, A.J. Heber. 2010. Field air sampling and simultaneous chemical and sensory analysis of livestock odorants with sorbent tubes and GC-MS/olfactometry. Sensors and Actuators B: Chemical. 146: 427-432.

[8] Willig, S., M. Lacorn and R. Claus. 2004. Development of a rapid and accurate method for the determination of key compounds of pig odor. Journal of Chromatography A. 1038:11–18.

[9] McGinn, S.M., H.H. Jantzen and T. Coates. 2003: Atmospheric ammonia, volatile fatty acids and other odorants near beef feedlots. Journal of Environmental Quality. Vol 32, pp 1173-1182, (2003).

[10] Banwart, W.L. and J.M. Bremner. 1975. Formation of volatile sulfur compounds by microbial decomposition of sulfur-containing amino acids in soils. Soil Biology and Biochemistry. 7(6): 359-364.

[11] Beard, W.L. & W.D. Guenzi. 1983. Volatile sulfur compounds from a redox-controlled cattle-manure slurry. Journal of Environmental Quality. 12: 113– 116.

[12] McGill, A.E.J. and N. Jackson. 1977. Changes in the short-chain carboxylic acid content and chemical oxygen demand of stored pig slurry. J. Sci. Food and Agric., 28: 424-30.

[13] Cooper, P. and I.S. Cornforth. 1978. Volatile fatty acids in stored animal slurry. J. Sci. Food and Agric., 29: 19-27.

[14] Spoelstra, S.F. 1980. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odour development. Agriculture and Environment. 5:241–260.

[15] Alanis, P., M. Sorenson, M. Beene, C. Krauter, B. Shamp, and A.S. Hasson. 2008. Measurement of non-enteric emission fluxes of volatile fatty acids from a California dairy by solid phase micro-extraction with gas chromatography/mass spectrometry. Atmospheric Environment. 42: 6417–6424.

[16] Blunden, J., V.P. Aneja, and W.A. Lonneman. 2005. Characterization of non-methane volatile organic compounds at swine facilities in eastern North Carolina. Atmospheric Environment. 39: 6707–6718.

[17] Defoer, N., I. De Bo, H. Van Langenhove, J. Dewulf, and T. Van Elst. 2002. Gas chromatography–mass spectrometry as a tool for estimating odour concentrations of biofilter effluents at aerobic composting and rendering plants. Journal of Chromatography A. 970: 259–273.

[18] Filipy, J., B. Rumburg, G. Mount, H. Westberg, and B. Lamb. 2006. Identification and quantification of volatile organic compounds from a dairy. Atmospheric Environment. 40: 1480–1494.

[19] Nielsen, A.T. and S. Jonsson. 2002. Quantification of volatile sulfur compounds in complex gaseous matrices by solid-phase microextraction. Journal of Chromatography A. 963: 57-64.

[20] Ras, M.R., F. Borrull, and R.M. Marc. 2008. Determination of volatile organic sulfur compounds in the air at sewage management areas by thermal desorption and gas chromatography–mass spectrometry. Talanta. 74: 562–569.

[21] Rabaud, N.E., S.E. Ebeler, L.L. Ashbaugh, R.G., Flocchini. 2003. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. Atmospheric Environment. 37: 933-940.
[22] Schiffman, S.S., J.L. Bennett, and J.H. Raymer. 2001. Quantification of odors and odorants from swine operations in North Carolina. Agricultural and Forest Meteorology. 108: 213-240.
[23] Sunesson, A.L., J. Gullberg, and G. Blomquist. 2001. Airborne chemical compounds on dairy farms. Journal of Environmental Monitoring. 3: 210–216.
[24] Kim, K-H., G-H. Choi, Y-J. Choi, H-N. Song, H-S. Yang, J-M. Oh. 2006. The effects of sampling materials selection in the collection of reduced sulfur compounds in air. Talanta. 68: 1713-1719.
[25] Trabue, S., K. Scoggin, F. Mitloehner, H. Li, R. Burns, and H. Xin. 2008. Field sampling method for quantifying volatile sulfur compounds from animal feeding operations. Atmospheric Environment. 42: 3332–3341.
[26] Koziel, J.A., J.P. Spinhirne, J.D. Lloyd, D.B. Parker, D.W. Wright, F.W. Kuhrt. 2005. Evaluation of Sample Recovery of Malodorous Livestock Gases from Air Sampling Bags, Solid-Phase Microextraction Fibers, Tenax TA Sorbent Tubes, and Sampling Canisters. Journal of the Air & Waste Management Association 55: 1147-1157.
[27] Feilberg, A., D. Liu, A.P.S. Adamsen, M.J. Hansen, K.E.N. Jonassen. 2010. Odorant emissions from intensive pig production measured by online proton-transfer-reaction mass spectrometry. Environ. Sci. Technol. 44: 5894-5900.
[28] Koziel, J.A., Y.M. Lo, L. Cai, D.W. Wright. 2010. Simultaneous characterization of VOCs and livestock odors using solid-phase microextraction – multidimensional gas chromatography – mass spectrometry-olfactometry. 23: 73-78.
[29] Huffel, K.V., P.M. Heynderickx, J. Dewulf, H.V. Langenhove. 2012. Measurement of odorants in livestock buildings: SIFT-MS and TD-GC-MS. Chemical Engineering Transactions. 30: 67-72.
[30] Lee, H., S. Jeon, W. Choi, S. Lee, M. Lee, K. Oh. 2013. A novel assessment of odor sources using instrumental analysis combined with resident monitoring records for an industrial area in Korea. Atmospheric Environment. 74: 277-290.
[31] Spinhirne, J.P., J.A. Koziel. 2003. Generation and Calibration of Standard Gas Mixtures for Volatile Fatty Acids using Permeation Tubes and Solid Phase Microextraction. Transactions of the ASABE, 46(6), 1639-1646.
[32] Koziel, J.A., P. Martos, and J. Pawliszyn. 2004. System for generation of standard gas mixtures of volatile and semivolatile organic compounds for calibrations of solid phase microextraction and other sampling devices. Journal of Chromatography A, 1025, 3-9.
[33] Meylan, W.M., P.H. Howard. 2005. Estimating octanol–air partition coefficients with octanol–water partition coefficients and Henry's law constants. Chemosphere. 61:640-644.
[34] Devos, M., F. Patte, J. Rouault, P. Laffort, L.J. Van Gemert. 1990. Standardized Human Olfactory Thresholds. Oxford University Press, New York
[35] Koziel, J. A., J. P. Spinhirne, J. D. Lloyd, , D. B. Parker, and D. W. Wright. 2004. Evaluation of sample recovery of malodorous gases from air sampling bags, SPME, and sampling canisters. ASAE Paper No. 044129. St. Joseph, Mich.: ASAE.
[36] Yang, X., J.A. Koziel, T. Cutler, S. Zhang, J. Zimmerman, S.J. Hoff, W. Jenks, J (Hans) van Leeuwen. 2008. Treatment of livestock odor and pathogens with ultraviolet light. Paper # 085198, ASABE Annual International Meeting. Providence, RH, June, 2008.
[37] Keszler, Á., K. Héberger. 1999. Influence of extraction parameters and medium on efficiency of solid-phase microextraction sampling in analysis of aliphatic aldehydes. J. Chromatogr. A 845: 337–347.
[38] Pawliszyn, J. 1997. SPME method development. In Solid Phase Microextraction; Theory and Practice; Pawliszyn, J., Ed.; Wiley-VCH: New York.
[39] Koziel, J. A., L. Cai, D. Wright, S. Hoff. 2006. Solid phase microextraction as a novel air sampling technology for improved, GC-Olfactometry-based, assessment of livestock odors. J. Chromatogr. Sci. 44(7): 451-457.
[40] Ripp, J. 1996. Analytical detection limit guidance and laboratory guide for determining method detection limits. Wisconsin Department of Natural Resources Laboratory Certification Program Report No. PUBL-TS-056-96. Madison, WI, USA, 30 pp.
[41] Cai, L., S. Zhang, J.A. Koziel, G. Sun, K.Y. Heathcote, S.J. Hoff, D.B. Parker, E. A. Caraway, L.D. Jacobson,

N. Akdeniz, B.P. Hetchler, E.L. Cortus, S.D. Bereznicki, A.J. Heber, T.T. Lim. 2012. Odor and Odorous Chemical Emissions from Animal Buildings: Part 3 – Chemical Emissions. Transactions of ASABE, submitted.

Figure Captions

Fig.1. A Scheme of the standard gas mixture generation system (SGG) coupled with a bench-scale UV photoreactor.

Fig.2. Comparison of extraction efficiency of target VOCs for different SPME fibers coatings: CAR/PDMS 85 µm, PDMS/DVB 65 µm, PDMS 100 µm and Polyacrylate 85 µm. MS detector response was normalized by gas concentrations. SPME conditions: T = 25 ºC, sampling time = 5 min, flow rate = 300 mL/min, dry air. Abbreviations: methyl mercaptan = MeSH, ethyl mercaptan = EtSH, dimethyl sulfide = DMS, n-butyl mercaptan = BM, acetic acid = AcOH, propanoic acid = PPA, butyric acid = BTA, isovaleric acid = IVA.

Fig.3. Optimization of SPME sampling time of target VOCs from standard gas mixture: normalized by gas concentrations. Experimental conditions: CAR/PDMS 85 µm SPME fiber, 300 mL/min standard gas flow, T=25 ºC, dry air. Five min sampling was selected for all follow-up experiments.

Fig.4. Calibration curves for target VOCs. Experimental conditions: gas sampling with CAR/PDMS 85 µm; 5 min sampling time; T=25 ºC; dry air.

Fig. 5. Comparison of total ion chromatograph of treated gas sample with control sample from SGG. Experimental conditions: gas sampling with CAR/PDMS 85 µm; 5 min sampling time; T=25 ºC; dry air; flow rate = 300 ml/min; UV treatment at 254 nm (principle) and 185 nm, with light intensity = 1.5 mW/cm^2 @254 nm with TiO_2 present. Note: MM=methyl mercaptan, EM=ethyl mercaptan, DMS=dimethyl sulfide, BM=butyl mercaptan, AA=acetic acid, PA= propanoic acid, BA=butyric acid, IV=isovaleric acid.